Evaluation of the long-term behaviour of potential plutonium wasteforms in a geological repository

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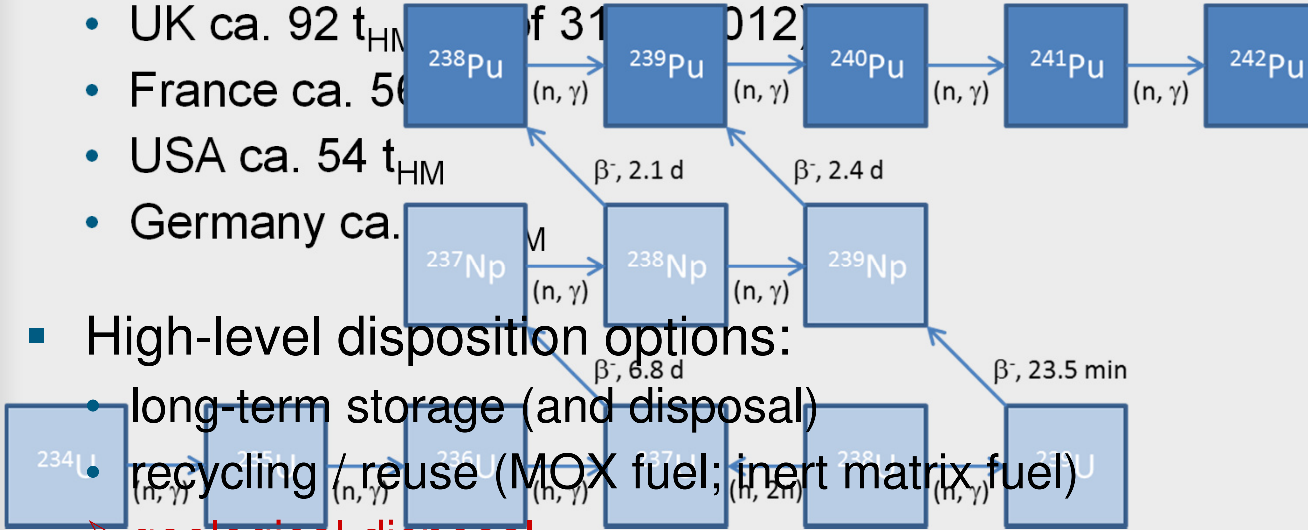
Background

- Plutonium (Pu)
  - forms in reactors using U-based fuels by various nuclear reactions (mainly n, γ)
  - separated during spent fuel reprocessing (e.g. PUREX process) and stored mainly as calcined PuO_2
  - isotopic composition variable depending on reactor type and fuel burn-up (predominantly Pu-239 and Pu-240)

- Stocks of separated civilian plutonium (2010)
  - UK ca. 92 t_{HM} … f 31 … 012)
  - France ca. 5…
  - USA ca. 54 t_{HM}
  - Germany ca. … M

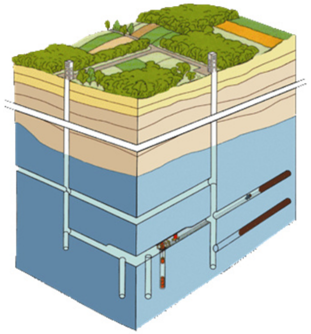
- High-level disposition options:
  - long-term storage (and disposal)
  - recycling / reuse (MOX fuel; inert matrix fuel)
  - ➢ geological disposal



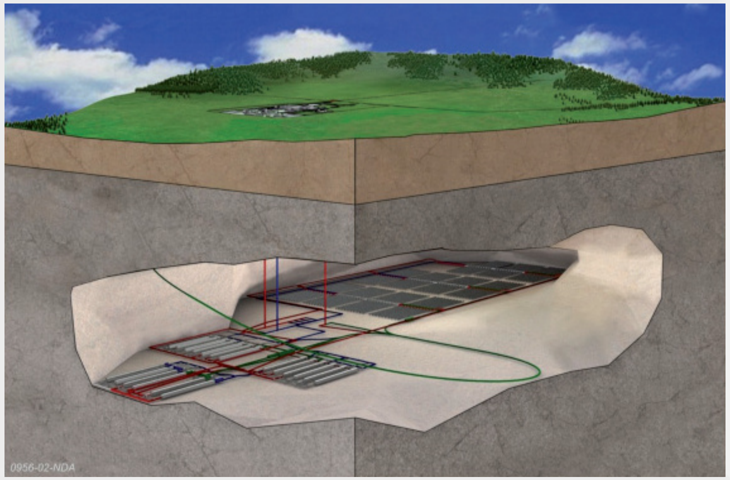
Wasteform issues for Pu disposal

Conversion

Geological Disposal



- Safety case issues for geological disposal
  - long-term durability of Pu wasteforms
  - long-term radionuclide release from Pu wasteforms under disposal conditions
  - post closure criticality events



Scope & Objectives

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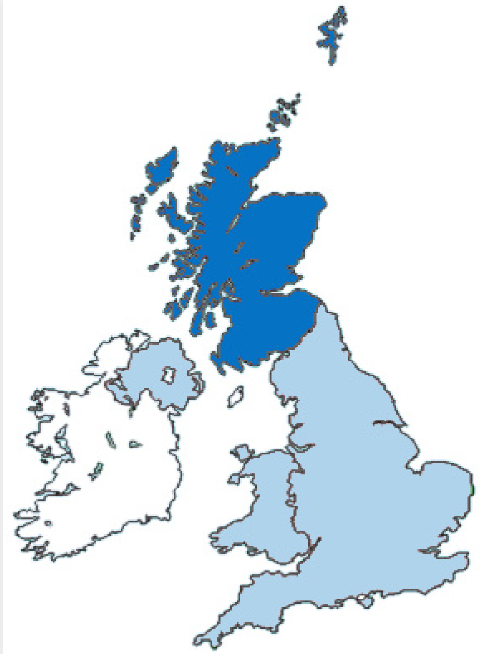
- NDA RWMD responsible for the implementation of geological disposal of higher activity wastes in the UK
- wastes to be managed through geological disposal:
  - HLW, ILW, LLW (if unsuitable for LLWR)

  and potentially
  - spent fuel (SF)
  - ➢ separated civil plutonium
  - uranium (DNLEU)

  if declared as wastes

NDA
Nuclear Decommissioning Authority



- Objectives:
  - Review and evaluation of performance and long-term behaviour of potential Pu wasteforms under repository conditions relevant for the UK
  - Corrosion rates / Pu release under disposal conditions
  - ➢ support decisions on Pu disposal in the UK

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Geological disposal in the UK

- UK geological disposal programme in generic stage
  - generic host rock types
  - illustrative disposal concepts (incl. co-disposal of LILW)

Parameter		"higher strength" crystalline rocks	"lower strength" sedimentary rocks	Evaporites
pH		near neutral	near neutral	~7.0
E_H	[mV]	< -200	< -200	< -200
dominant cations		Na	Na, Ca	Na (Ca)
Cl^-	[mg L^{-1}]	13,000 … 104,000	5,600 … 104,000	~200,000
SO_4^{-2}	[mg L^{-1}]	1,000 … 3,400	2,300 … 3,400	3,000
HCO_3^-	[mg L^{-1}]	< 100	100 … 200	50

Watson et al. 2007, King 2009

Potential Pu wasteforms

Glasses

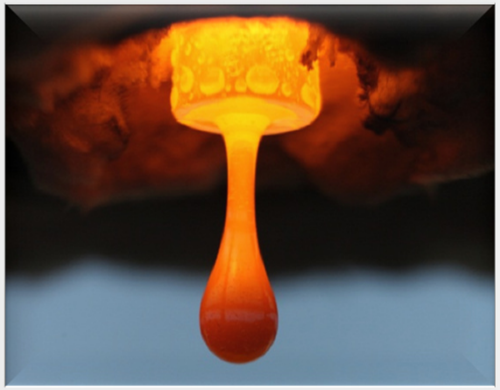
Glass ceramics

Ceramics

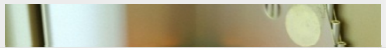
Storage MOX

Encapsulants

- Borosilicate glasses
  - lanthanide borosilicate
  - lead borosilicate
  - calcium borosilicate
- Alkali-Tin-Silicate glasses
- Phosphate glasses
  - iron phosphate
  - aluminium phosphate



- Low-specification ("storage") MOX
  - MOX fuel not destined for reactor usage (fabricated by established technology)
  - reduced technological specifications
  - higher Pu load compared



- Cements
- Polymers

Evaluation of wasteform performance

- Focal points:
  - durability in aqueous environments
  - wasteform stability/integrity over geological time scales (effects of radiation damage, helium build-up)
  - criticality control

? Sufficient information available for the assessment of the long-term behaviour and performance of the wasteforms ?

- Key controls of wasteform performance:

➢ intrinsic (wasteform)
- plutonium loading
- mode of Pu incorporation
- chemical/mineralogical composition
- radiation tolerance
- mechanical stability

➢ extrinsic (repository environment)
- hydrogeology (advective vs. diffusive flows)
- geochemical conditions (pH, E_H, T, I, A^+, B^-, …)
- microbial activity

↳ dependent on repository design (EBS) and host rock

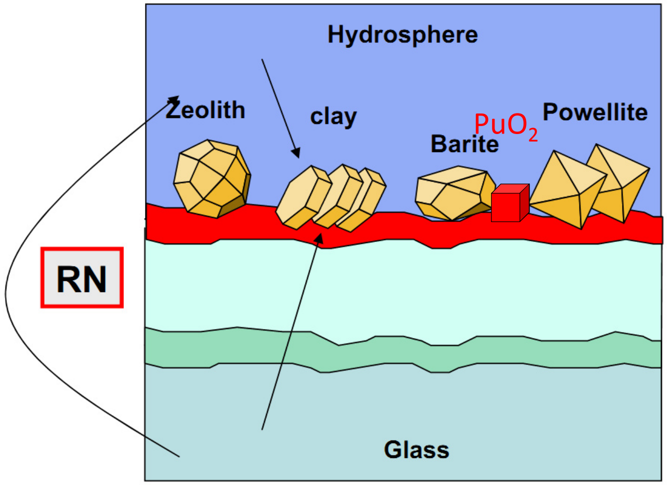
Glass wasteforms for Pu

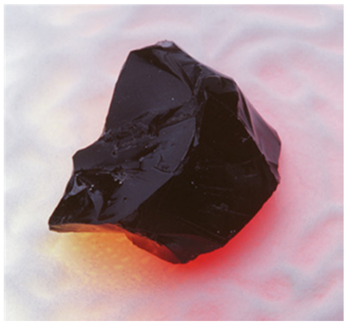
- comparatively few studies on the durability of Pu waste glasses compared to HLW glasses
- focus mainly on borosilicate / LnBS glasses
- leaching experiments mainly with standardised tests (MCC, PCT) using deionised water, mainly with surrogates (Ce, Hf), few long-term tests

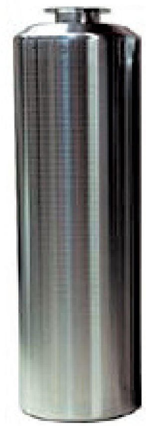
➢ leaching rates for Pu (or surrogates) significantly lower than for glass matrix elements (e.g. B, Si, etc.)

➢ Pu (and surrogates) retained in secondary phases

➢ no effect of radiation dose on Pu release observed for borosilicate glass





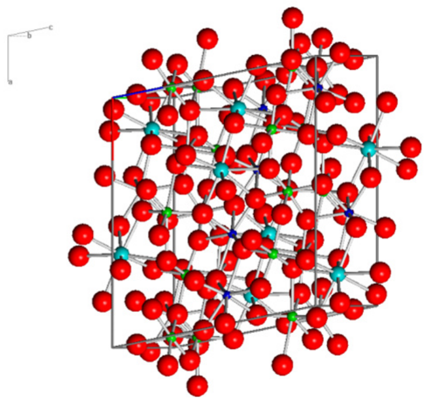


Ceramic wasteforms for Pu

- investigations performed on various polyphase and singlephase ceramics for actinide/Pu immobilisation
- leaching experiments often with standardised tests (MCC, PCT) using deionised water or under acidic conditions, often with surrogates (Ce, Hf, Nd), long-term tests rare

➢ leaching rates are orders of magnitude lower compared to glasses with rates for Pu (and surrogates), Ti and Zr often ~10^{-5} g m^{-2} d^{-1} or less

➢ different response to self-irradiation
  - no amorphisation of monazite and Zr-pyrochlore
  - no effect of radiation dose on durability observed for some metamict zirconolites



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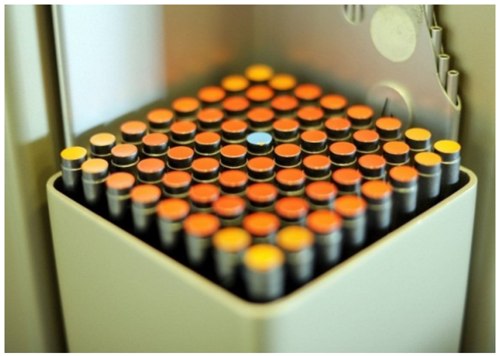
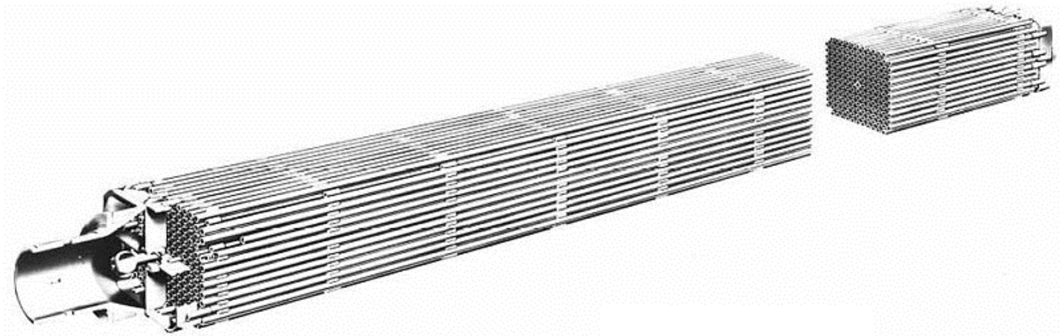
Storage MOX as a wasteform

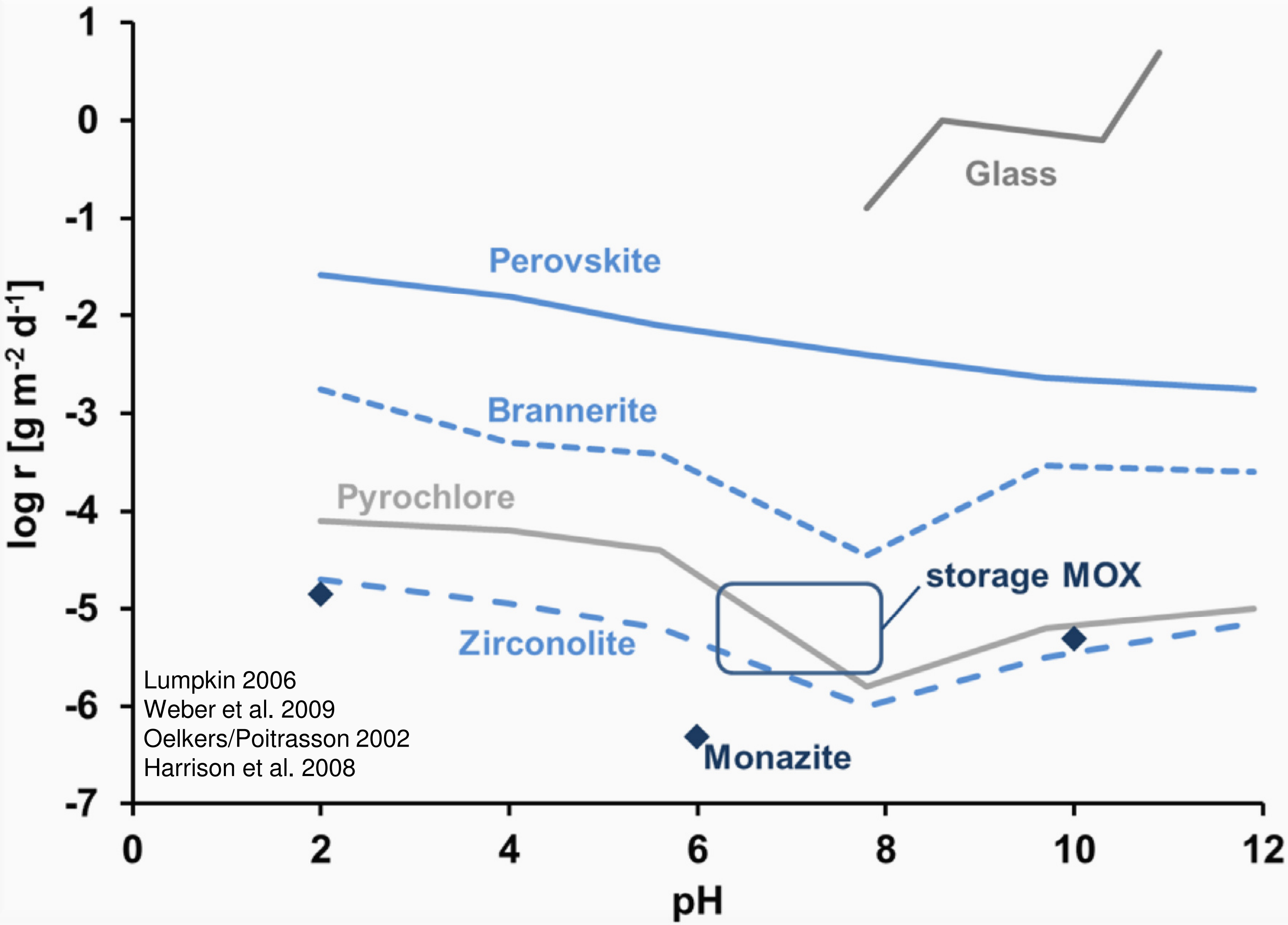
- concept has received considerably less attention than immobilisation of plutonium in glasses and/or ceramics
- very limited information on wasteform behaviour available

- short-term static leaching tests in deionised water, granitic water and carbonated water suggest leaching rates around 10^{-5} g m^{-2} d^{-1}
- Pu leaching rates under reducing conditions lower than for uranium
- high durability under reducing (long-term) conditions in a GDF inferred





Key findings



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Performance under disposal conditions

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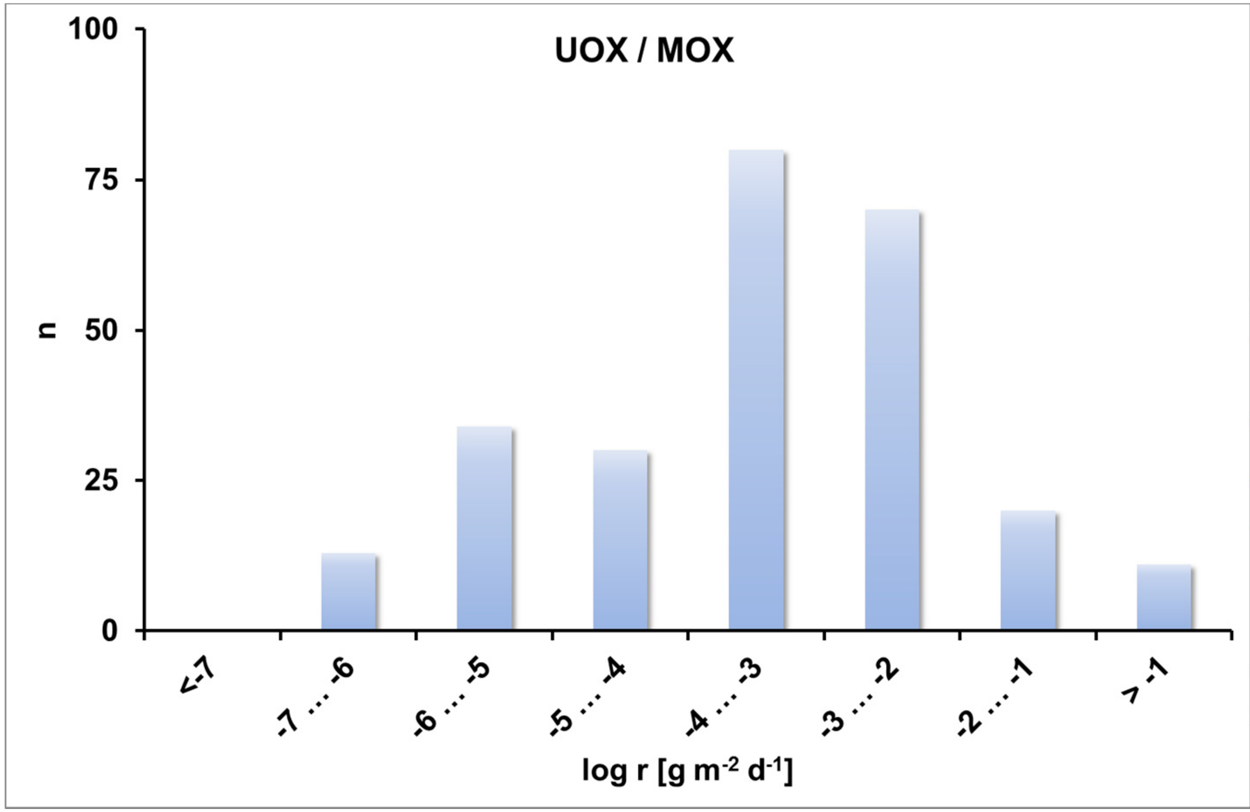
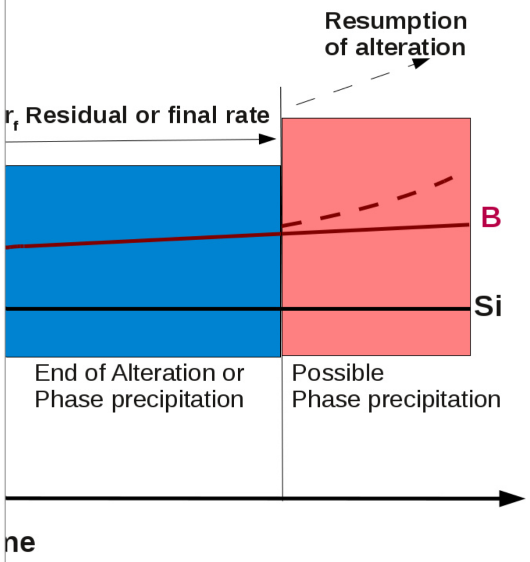
- Assessment of corrosion rates of Pu wasteforms in a GDF?
  - understanding of wasteform behaviour
  - information for PCSA
  - safety margins of highly durable matrices
  - potential for post-closure criticality events (leaching of neutron absorbers)
  - evaluation of disturbed repository evolution scenarios (human intrusion, tectonic events/fracturing)

- Derivation of “bounding values” for corrosion rates under UK disposal conditions based on
  - experimental data from Pu wasteforms
  - analogue evidence (e.g. HLW-glasses, spent UOX/MOX)
- Generic wasteform types
  - “glasses”
  - “ceramics”
  - “storage MOX”
- near-field conditions: pH 7 … 13; low/high salinity, …

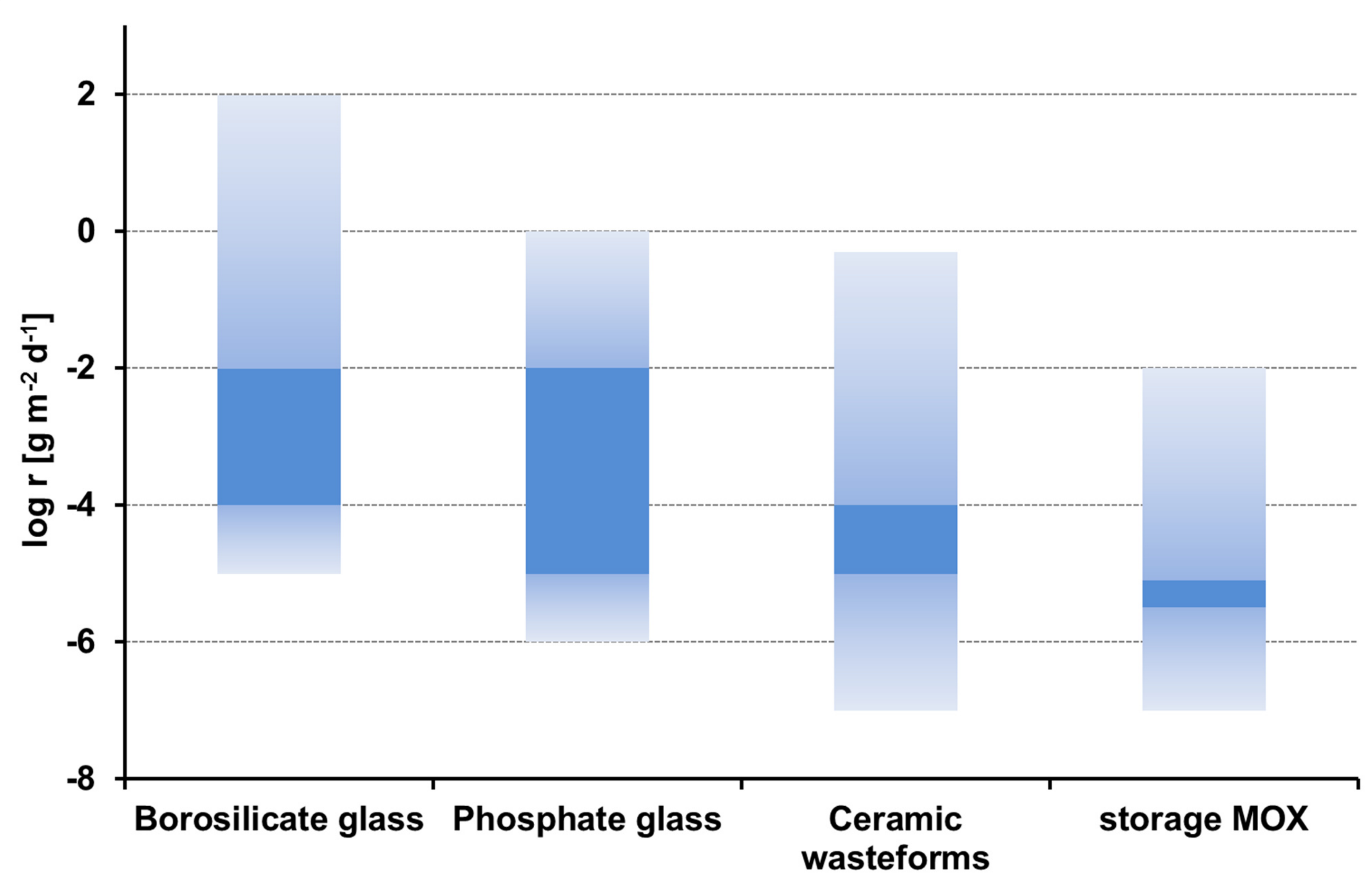
Derivation of corrosion rates

- storage MOX:
  - ➢ analogue SF/MOX matrix alteration (e.g. SFS, NF-PRO, MICADO)
  - conservative “upper bound”: oxidative/radiolytic SF dissolution
  - non-conservative “lower bound”: long-term SF dissolution rates (H_2 overpressure)
  - best estimate: SF dissolution rates, reducing conditions





Durability under disposal conditions



Conclusions & Outlook

- Information on the long-term behaviour and durability of plutonium wasteforms under disposal conditions rather limited compared to HLW-glasses and spent fuel
  - available information is focussed mainly on ceramics and glasses
  - ceramic wasteforms (and MOX) look promising with respect to aqueous durability
  - detailed understanding of relevant processes that govern wasteform corrosion, radionuclide release and total systems behaviour seems to be still missing

- Bounding values for plutonium wasteform corrosion rates under repository conditions can be derived from available experimental data and analogue evidence
- However:
  more realistic assessments of wasteform durability and radionuclide release behaviour would require systematic studies regarding
  - Pu wasteform corrosion under realistic conditions
  - secondary phases formed during Pu wasteform corrosion
  - effects of self-irradiation on wasteform performance/durability

  to explore the safety margins of the various potential wasteforms

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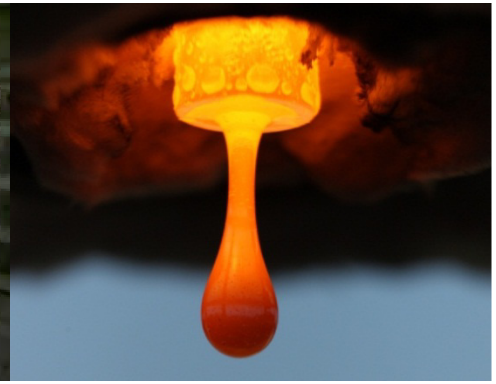
The End



Thanks to

- NDA RWMD: for funding this project

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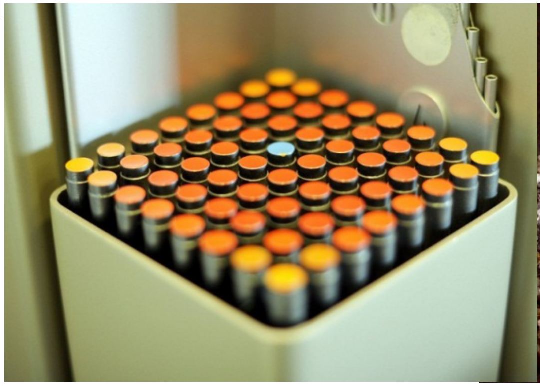
- The Audience: for kind attention



Questions???

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